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CITATION:

Einaga, Yoshiyuki. A Thermodynamic Approach to Phase Equilibrium in Ternary Polymer Solutions (Commemoration Issue Dedicated to Professor Hiroshi Ibagaki, Professor Michio Kurata, Professor Ryoza Kitamura, On the Occasion of Their Retirements). Bulletin of the Institute for Chemical Research, Kyoto University 1989, 66(3): 140-153

ISSUE DATE:

1989-02-15

URL:

<http://hdl.handle.net/2433/77247>

RIGHT:

A Thermodynamic Approach to Phase Equilibrium in Ternary Polymer Solutions

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Received August 25, 1988

A new approach to the phase separation phenomena in ternary polymer solutions was employed to describe the phase diagrams of the ternary systems polystyrene+polyisobutylene+cyclohexane, polystyrene+polyisobutylene+benzene, and polystyrene+cyclohexane+N, N dimethylformamide. The theoretical predictions of the phase relationships were favorably compared with the experimental results for the binodal curves and tie lines, thereby proving that the new treatment of the phase problem was applicable to both the polymer+polymer+solvent and polymer+solvent+solvent ternary systems.

KEY WORDS: Thermodynamics/ Phase Equilibrium/ Ternary Polymer Solution/

INTRODUCTION

Phase relationships in the ternary system consisting of two chemically different polymers and one solvent or one polymer and two solvents are subtly dependent on the interactions between different components. It is a long-standing problem in the field of polymer solution studies since the pioneering work by Scott¹⁾ and Tompa²⁾ in the late 1940s to describe or predict theoretically such involved phase separation phenomena. The pioneers applied the Flory-Huggins formulation for the Gibbs free energy of mixing ΔG to the problem, by extending the original expression for binary polymer solutions to that for ternary systems. It reads:

$$\Delta G/RT = (N_0 + \sum_{i=1}^2 N_i P_i) (\phi_0 \ln \phi_0 + \sum_{i=1}^2 P_i^{-1} \phi_i \ln \phi_i + h) \quad (1)$$

$$h = \chi_{01} \phi_0 \phi_1 + \chi_{02} \phi_0 \phi_2 + \chi_{12} \phi_1 \phi_2 \quad (2)$$

where R is the gas constant, T the absolute temperature, N_i and ϕ_i the amount and the volume fraction of species i , and the function h represents interactions among components in a given system. The parameter χ_{ij} was introduced to account for the interaction between components i and j , and regarded as a constant or a function of temperature only. The approach based on these equations has long been applied to a variety of ternary polymer systems as reviewed in the intriguing book by Kurata.³⁾

Although the treatment qualitatively explains the observed phase behavior, the estimated phase diagrams⁴⁻⁶⁾ are usually far from the actual ones in a quantitative sense. The thermodynamic state of the polymer system has to be given in greater detail than the simple theoretical presumptions about χ_{ij} stated above. Many studies^{3,7-9)} on binary polymer solutions have unequivocally established that the interaction parameter is in general a function of polymer concentration and molecular weight

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as well as temperature. It should be the case for ternary polymer solutions. Thus, for the accurate prediction of phase relations we have to know the dependence of ΔG on all relevant variables. To meet this requirement, Koningsveld et al.¹⁰⁾ put the interaction function h in the general form as

$$h = g_{01}(\phi_1, \phi_2)\phi_0\phi_1 + g_{02}(\phi_1, \phi_2)\phi_0\phi_2 + g_{12}(\phi_1, \phi_2)\phi_1\phi_2 \quad (3)$$

This equation is, however, of no practical use, since it includes three unknown functions g_{ij} which involve the same composition variables and then cannot be determined separately.

Recently, we have proposed a new approach to the phase problem in ternary polymer solutions.¹¹⁻¹³⁾ The treatment is not molecular theoretical but completely phenomenological or thermodynamic. Though we also use eq 1 as the basic equation to express ΔG of the actual ternary system, we do not adhere to its literal conception. The hypothetical solution whose ΔG is represented by the first two terms in eq 1 is taken as a mere reference system and the interaction function h lumps all the deviation of a given ternary solution from the reference.

This paper describes the theoretical framework of our approach and the results applied it to the systems polystyrene (PS)+polyisobutylene (PIB)+cyclohexane (CH), PS+PIB+benzene, and PS+CH+N, N dimethylformamide (DMF). The main aim is to demonstrate that our new treatment is effective for both the polymer+polymer+solvent and polymer+solvent+solvent ternary systems.

THERMODYNAMICS OF TERNARY POLYMER SOLUTIONS

This section briefly summarizes the essentials of our approach to the thermodynamics of ternary polymer solutions.

(a) Chemical Potential

We define the interaction function χ through the chemical potential μ_0 of the solvent (component 0) by the equation

$$(\mu_0 - \mu_0^0)/RT = \ln \phi_0 + (1 - P_n^{-1})\phi + \chi\phi^2 \quad (4)$$

which is derived from eq 1. Here μ_0^0 is the value of μ_0 of the pure solvent, ϕ the overall volume fraction of the solutes $\phi = \phi_1 + \phi_2$, and P_n the number-average relative chain length of the solute mixture defined by

$$P_n^{-1} = \xi_1 P_1^{-1} + \xi_2 P_2^{-1} \quad (5)$$

with $\xi_i = \phi_i/\phi$ and $P_i = V_i/V_0$, V_i being the molar volume of the component i . The interaction function χ is related to the h function by

$$\chi = -[\partial(h/\phi)/\partial\phi]_{T, \xi_i} \quad (6)$$

The Gibbs-Duhem relation and eq 4 give

$$(\mu_i - \mu_i^\infty)/RT = \ln \phi_i + P_i(1 - P_n^{-1})\phi - P_i \int_0^\phi \chi d\phi + (1 - \xi_i) \int_0^\phi (\partial\chi/\partial\xi_i) d\phi$$

$$+ \chi \phi_0 \phi] \quad (i=1, 2) \quad (7)$$

for the chemical potential μ_i of component i , with the aid of the condition

$$\mu_i^\infty = \lim_{\phi \rightarrow 0} (\mu_i - RT \ln \phi_i) \quad (i=1, 2) \quad (8)$$

The quantity μ_i^∞ is independent of the composition of the solution and a function of T only as is the case with the chemical potential μ_i^o of solute i at the pure state. Equation 7 is the expression of μ_i when the standard state is taken at the infinite dilution of the solute components. The h function can be derived from eqs 6 and 7 as

$$h/\phi = - \int_0^\phi \chi d\phi + \sum_{i=1}^2 \xi_i [(\mu_i^\infty - \mu_i^o)/P_i RT - 1/P_i + 1] \quad (9)$$

The compositions of two conjugate phases (signified by single and double primes) can be determined by the phase equilibrium conditions, i.e., $\mu'_0 = \mu''_0$ and $\mu'_i = \mu''_i$ ($i=1, 2$). The condition $\mu'_i = \mu''_i$ is conveniently represented in terms of the separation factor σ_i defined by

$$\sigma_i = P_i^{-1} \ln (\phi''_i / \phi'_i) \quad (10)$$

With eqs 4 and 7, it can be shown that ∂_i is expressed as

$$\sigma_i = \Delta | \ln \phi_0 + \chi \phi + \int_0^\phi [\chi + (1 - \xi_i)(\partial \chi / \partial \xi_i)] d\phi | \quad (11)$$

where $\Delta | X |$ denotes the difference $X'' - X'$.

(b) General Expression of χ

According to Kurata,³⁾ the osmotic pressure π^* of the ternary polymer solution containing two polymer components 1 and 2 at constant T and μ_0 , can be expanded in powers of polymer mass concentration c_1 and c_2 as

$$\pi^* / RT = -(\mu_0 - \mu_0^o) / V_0 RT \\ = \sum_{i=1}^2 c_i / M_i + \frac{1}{2} \sum_{i=1}^2 \sum_{j=1}^2 B_{ij} c_i c_j + \frac{1}{3} \sum_{i=1}^2 \sum_{j=1}^2 \sum_{k=1}^2 B_{ijk} c_i c_j c_k + \dots \quad (12)$$

where M_i is the molecular weight of polymer i and B_{ij}, \dots the interaction coefficients invariant with exchange of subscripts. Substitution of eq 4 into eq 12 leads to

$$\chi = \xi_1^2 (D_{11} + D_{111} \phi_1 + D_{1111} \phi_1^2 + \dots) \\ + \xi_2^2 (D_{22} + D_{222} \phi_2 + D_{2222} \phi_2^2 + \dots) \\ + 2 \phi_1 \phi_2 [D_{12} + \frac{3}{2} (D_{112} \phi_1 + D_{122} \phi_2) + \dots] \quad (13)$$

with

$$D_{ij} = \frac{1}{2} (1 - V_0 B_{ij} / v_i v_j), \quad D_{ijk} = \frac{1}{3} (1 - V_0 B_{ijk} / v_i v_j v_k), \dots \quad (14)$$

Here v_i is the partial specific volume of component i and it is assumed that v_0 is independent of composition and pressure.

For $\xi_i=1(i=1, 2)$, eq 13 is reduced to

$$\chi = D_{ii} + D_{iii}\phi + D_{iiii}\phi^2 + \dots \quad (15)$$

If this quantity is denoted by $\chi_{ii}(\phi)$, the first and second terms in eq 13 can be expressed as $\xi_1^2\chi_{11}(\phi_1)$ and $\xi_2^2\chi_{22}(\phi_2)$, respectively. Then, we finally arrive at

$$\chi = \xi_1^2\chi_{11}(\phi_1) + \xi_2^2\chi_{22}(\phi_2) + 2\xi_1\xi_2\chi_{12}(\phi_1, \phi_2) \quad (16)$$

which is the general expression of χ we wanted to derive, where

$$\chi_{12}(\phi_1, \phi_2) = D_{12} + \frac{3}{2}(D_{112}\phi_1 + D_{122}\phi_2) + \dots \quad (17)$$

Equation 15 corresponds to the interaction function for the binary solution consisting of solute i and solvent 0. The first and second terms in eq 16 can be, thus, determined from thermodynamic measurements for the corresponding binary systems, since they include only ϕ_i as the composition variable. As can be understood from eqs 15 and 17 together with the relation 14, the present χ_{ij} represents the interactions between solute components i and j in a given solvent, differing from the conventional interaction parameter based on the lattice theory. It should be noted that eq 16 holds also for the polymer+solvent+solvent ternary systems, if one of the two solvents is regarded as a solute.

(c) Light Scattering Equation

Light scattering serves as a powerful tool for evaluating the interaction function of ternary and binary polymer solutions. The forward excess Rayleigh ratio ΔR_0 due to concentration fluctuation in ternary systems can be derived in terms of the interaction function χ from the general theory of light scattering.^{3,12)} The final result is

$$KV_0\phi/\Delta R_0 = [1 + \phi(1-\phi)^{-1}P_w - \phi(P_wL + Y)]/WX \quad (18)$$

$$W = (\bar{\gamma}_1^2 P_1 \xi_1 + \bar{\gamma}_2^2 P_2 \xi_2)/(1-\phi)^2 \quad (19)$$

$$\begin{aligned} X = & 1 + (\bar{\gamma}_1^2 P_1 \xi_1 + \bar{\gamma}_2^2 P_2 \xi_2)^{-1} \xi_1 \xi_2 [\bar{\gamma}_1 - \bar{\gamma}_2]^2 P_1 P_2 [1 + (P_n^{-1} - 1)\phi] \phi \\ & - 2(\bar{\gamma}_1 - \bar{\gamma}_2)(\bar{\gamma}_1 P_1 - \bar{\gamma}_2 P_2)\phi - (\bar{\gamma}_1 - \bar{\gamma}_2)^2 P_1 P_2 (1-\phi)^2 \phi L \\ & + 2(\bar{\gamma}_1 - \bar{\gamma}_2)(\bar{\gamma}_1 \xi_1 + \bar{\gamma}_2 \xi_2) P_1 P_2 (1-\phi)\phi M + (\bar{\gamma}_1 \xi_1 + \bar{\gamma}_2 \xi_2)^2 P_1 P_2 N \} \end{aligned} \quad (20)$$

$$Y = \xi_1 \xi_2 [2(P_1 - P_2)M - P_1 P_2 [(1-\phi)^{-1} + (P_n \phi)^{-1} - L]N + P_1 P_2 \phi M^2] \quad (21)$$

and

$$P_w = P_1 \xi_1 + P_2 \xi_2 \quad (22)$$

$$\bar{\gamma}_i = \gamma_i - \sum_{j=1}^2 \phi_j \gamma_j, \quad \gamma_i \equiv (\partial n / \partial \phi_i)_{\phi_k} \quad (23)$$

$$L \equiv 2\chi + \phi(\partial\chi/\partial\phi)_{\xi_i}, \quad M \equiv (\partial\chi/\partial\xi_1)_{\phi}, \quad N \equiv - \int_0^\phi (\partial^2\chi/\partial\xi_1^2) d\phi \quad (24)$$

where K is the optical constant and γ_i the refractive index increment. Substituting eq 16 into eq 18, we obtain ΔR_0 as a function of the interaction functions χ_{11} , χ_{22} , and χ_{12} .

For the binary solution of solute i +solvent 0, eq 18 reduces to

$$K\gamma_i^2 V_0/\Delta R_0 = 1/(1-\phi) + 1/(P_i\phi) - L_{ii} \quad (25)$$

where L_{ii} is the L function defined in eq 24 and related to χ_{ii} by

$$\chi_{ii}(\phi_i) = (1/\phi_i^2) \int_0^{\phi_i} L_{ii} \phi_i d\phi_i \quad (26)$$

Thus, eq 25 allows $\chi_{ii}(\phi_i)$ to be determined from measurement of $\Delta R_0(\phi)$ for the binary solution. Once $\chi_{11}(\phi_1)$ and $\chi_{22}(\phi_2)$ are obtained as functions of ϕ_1 and ϕ_2 , respectively, eq 18 becomes an integro-differential equation of $\chi_{12}(\phi, \xi_1)$. In principle, we can, thus, evaluate $\chi_{12}(\phi, \xi_1)$ from the light scattering data for the ternary polymer solution by using eq 18.

Finally, the phase equilibrium conditions, i.e., $\mu'_0 = \mu''_0$, eqs 10, and 11, combined with the interaction functions $\chi_{11}(\phi_1)$, $\chi_{22}(\phi_2)$, and $\chi_{12}(\phi, \xi_1)$ so determined, allow us to calculate the phase diagrams of the ternary system under consideration. This is the maneuver we have taken in the present and previous work on phase separation phenomena in ternary polymer solutions.

APPLICATION TO THE ACTUAL TERNARY POLYMER SOLUTIONS

In the present work, we designate PS as component 1, PIB as component 2, and the solvent CH or benzene as component 0 for the PS+PIB+CH or PS+PIB+benzene system. For the PS+CH+DMF system, we regard DMF as the solute (component 2), CH as the solvent (component 0), and PS as the solute component 1. The PS samples (F4a, F4b) and the PIB samples (U1, U2) in these systems are sufficiently narrow in molecular weight distribution. Their weight-average molecular weights M_w are 53600 for F4a, 51000 for F4b, 154000 for U1, and 152000 for U2. The relative chain length P_i of solute i is calculated by

$$P_i = M_i v_i / M_0 v_0 \quad (27)$$

where M_i and v_i are the molecular weight and specific volume of component i , respectively. The total volume fraction ϕ of the solute mixture in the ternary solution is obtained from the total weight fraction w by

$$\phi = [1 + v_0(\omega_1 v_1 + \omega_2 v_2)(w^{-1} - 1)]^{-1} \quad (28)$$

where ω_i is the weight fraction of component i in the solute mixture.

The volume fraction ξ_1 of component 1 in the solute mixture is related to ω_1 by

$$\xi_1 = [1 + (v_2/v_1)(\omega_1^{-1} \times 1)]^{-1} \quad (29)$$

A similar relation holds between ξ_2 and ω_2 . Note that $\xi_1 + \xi_2 = 1$. The volume fraction ϕ_i of component i in the ternary solution is given by $\phi \xi_i$. For the value of v_i ($\text{cm}^3 \text{g}^{-1}$), we use 0.9343 for PS,¹⁴⁾ 1.0906 for PIB,¹⁵⁾ 1.2923 for CH,¹⁶⁾ 1.1446 for benzene,¹⁶⁾ and 1.0594 for DMF¹⁷⁾ irrespective of the temperature of the solution examined, though all these values refer to 25°C. It should be, thus, noted that the experimental ϕ , ξ_i , and ϕ_i are not the volume fractions in the usual sense but the converted weight fractions.

I. Polystyrene+Polyisobutylene in Cyclohexane and in Benzene

a. Interaction Functions

According to the maneuver developed in the previous section, we need the interaction functions $\chi_{ii}(\phi_i)$ for the binary systems PS+CH, PIB+CH, PS+benzene, and PIB+benzene to determine the interaction function χ for the ternary systems. Among these, the χ_{11} equation for the PS+CH system has been already established by Einaga et al.¹⁸⁾ The other functions of L_{ii} or χ_{ii} were obtained from the light scattering or osmotic pressure data for the relevant binary solutions.¹⁹⁾ The empirical equations for these quantities are summarized as follows:

For PS+CH,

$$L_{11}(\phi_1) = 2[\chi_c^0 + \phi_1/2 + A\phi_1^4/(1 + B\phi_1^2) + (\chi_d^0 - \chi_c^0)R(P_1^{1/2} \phi_1)] \quad (30)$$

$$\begin{aligned} \chi_c^0 &= 0.4930 + 0.345(\theta/T - 1) + (-0.075P_1^{1/2} - 45P_1^{-2} + 0.007) \\ &\quad \exp[-(40 - 520P_1^{-2/3})(\theta/T - 1)] \end{aligned} \quad (31)$$

$$\chi_d^0 = 0.5 + 0.26(\theta/T - 1) + 4.6(\theta/T - 1)^2 \quad (32)$$

$$A = 1.4P_1^{1/2} \quad (33)$$

$$B = 7P_1^{1/3} \exp[-18(\theta/T - 1)] \quad (34)$$

$$R(x) = \exp(-x - 0.3x^3) \quad (35)$$

where θ is the theta temperature (307.65K).

For PIB(U1)+CH,

$$L_{22}(\phi_2) = 0.13 + 0.0017T + 6\phi_2^2 + (1.05 - 0.0017T - 90/T) \exp(-15\phi_2) \quad (36)$$

For PS(F4a)+benzene,

$$L_{11}(\phi_1) = 0.82 + 0.48\phi_1 + 5\phi_1^2 + (-0.36 + 0.00136T) \exp(-26\phi_1) \quad (37)$$

For PIB(U2)+benzene,

$$\chi_{22}(\phi_2) = 0.5 + 0.34(\theta/T - 1) + [0.29 + 0.72(\theta/T - 1)]\phi_2 + 0.2\phi_2^2 \quad (38)$$

with $\theta = 297.65K$.

The light scattering data for the ternary solutions were analyzed with eq 18 to obtain the interaction function χ_{12} . Equation 18, however, provides only an integro-differential equation of χ_{12} after the above equations for χ_{ii} were substituted, and does not allow direct evaluation of χ_{12} at finite solute concentrations. We, therefore, assumed a working equation

$$\chi_{12} = k_0 + (k_1\xi_1 + k_2\xi_2)\phi \quad (39)$$

which might be regarded as a truncated form of the general expansion of χ_{12} in powers of ϕ , i.e., eq 17. Substitution of eq 39 into eq 18 yields an expression of $KV_0\phi/\Delta R_0$ in terms of k_0 , k_1 , and k_2 . We evaluated k_0 , k_1 , and k_2 by the trial-and-error method so as to give the best agreement between calculated and observed values of $KV_0\phi/\Delta R_0$. The results are

$$k_0 = 0.348 + 30/T, \quad k_1 = -4.5 + 1507/T, \quad k_2 = -0.9 \quad \text{for PS+PIB+CH} \quad (40)$$

and

$$k_0 = 0.454, \quad k_1 = -0.7, \quad k_2 = 0.10 \quad \text{for PS+PIB+benzene} \quad (41)$$

Figure 1 illustrates a typical example of the comparison between calculated and observed values of $KV_0\phi/\Delta R_0$ for the PS+PIB+benzene solutions at various composition and temperatures. It is seen that the observed ϕ dependence of $KV_0\phi/\Delta R_0$ significantly varies with the composition of the polymer mixture. At $\xi_1 (= \xi_{PS}) \approx 0.5$, the data set at fixed T follows a curve convex upward and approaches zero at high concentrations with increasing ϕ . This behavior suggests that the solution approaches the spinodal concentration at that T and ξ_1 . On the other hand, $KV_0\phi/\Delta R_0$ at $\xi_1 \approx 0.9$ monotonically increases up to the highest ϕ examined, which is very close to the cloud point concentration. This result implies that there is a significant gap between cloud point and spinodal concentrations at $\xi_1 \approx 0.9$. The calculated curves well represent these features of the experimental $KV_0\phi/\Delta R_0$ values as a function of ϕ , ξ_1 , and T .

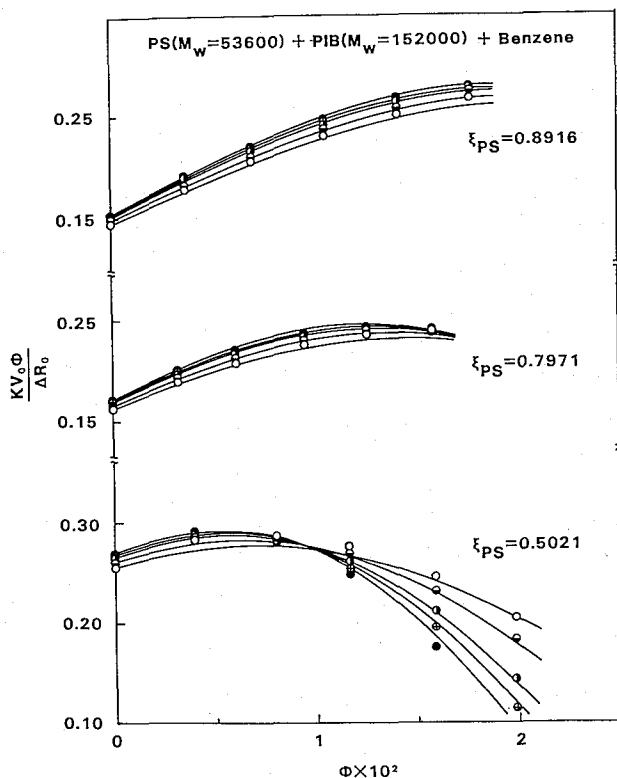


Figure 1. Plots of $KV_0\phi/\Delta R_0$ vs ϕ for the PS (F4a)+PIB (U2) mixtures of indicated ξ_{PS} in benzene. \circ , 35; \bullet , 30; \ominus , 25; \oplus , 23; \bullet , 21°C. Solid lines, calculated values.

b. Phase Diagram

Figure 2 and 3 depict the phase diagrams obtained both theoretically and experimentally for the PS+PIB+CH and PS+PIB+benzene systems, respectively. The experimental results clearly indicate that the phase separation behavior in the ternary systems is affected not only by the polymer-polymer repulsive interaction but also by the solvent property. The binodal curves spread out from a point near the solvent apex toward the polymer-polymer edge of the composition triangle, asymptotically approaching the $\phi_1 (= \phi_{PS})$ and $\phi_2 (= \phi_{PIB})$ axes with increasing ϕ . This observation qualitatively agrees with the experimental findings²⁰⁻²³⁾ reported for an incompatible polymer pair in a common good solvent. It is, thus, concluded that the main thermodynamic factor leading to this type of phase separation is the repulsive interaction between the incompatible polymer components.

The solvent effect on the phase diagrams appears in the shape of the binodal curves and the direction of the tie lines. In the two systems shown in Figures 2 and 3, use is made of the same PS sample and the PIB samples of approximately equal M_w . It is still seen that the change of the solvent from CH to benzene leads to significant variation in the shape of the binodal curve and the inclination of the tie lines. The binodal curves are distorted toward the edge representing the binary system of the

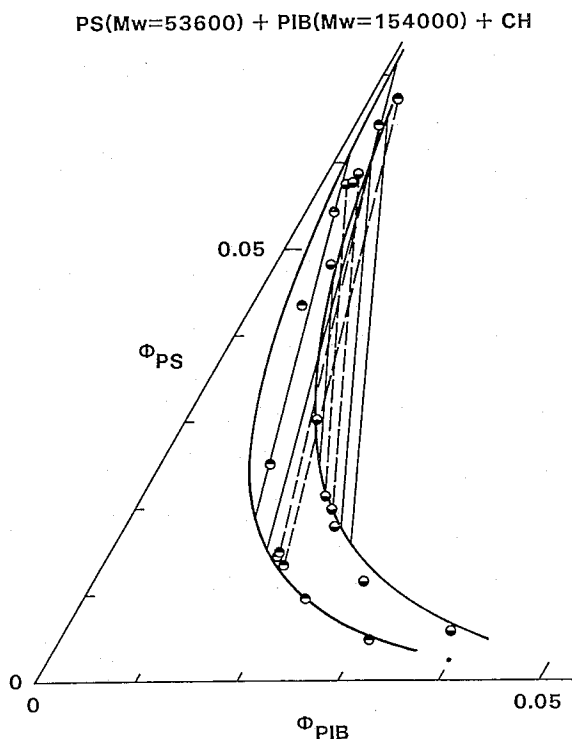


Figure 2. Binodals and tie lines for the PS (F4a)+PIB (U1)+CH system. Circles, observed binodals: ○, 30; ●, 20°C. Thick solid curves, calculated binodals; dashed lines, observed tie lines; thin solid lines, calculated tie lines.

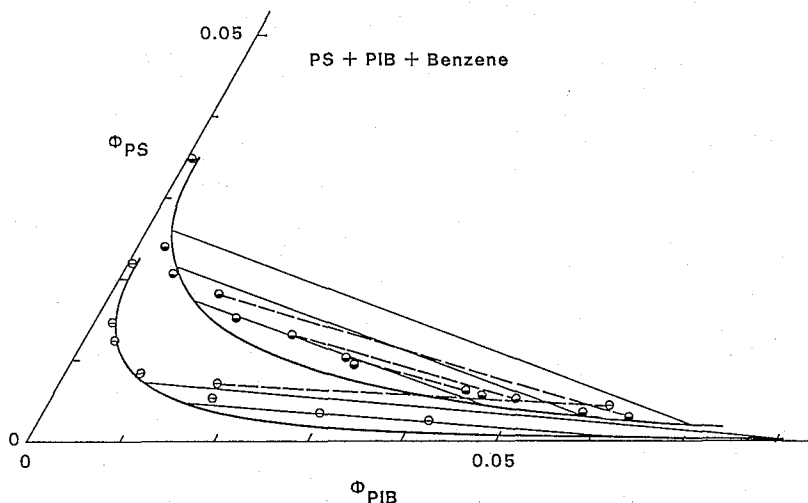


Figure 3. Binodals and tie lines for the PS (F4a)+PIB (U2)+ benzene system. Circles, observed binodals: \bullet , 30; \circ , 20°C. Thick solid curve, calculated binodals; dashed lines, observed tie lines; thin solid lines, calculated tie lines.

polymer+good solvent. The tie lines are significantly tilted to the ϕ_{PS} axis in the PS+PIB+CH system and to the ϕ_{PIB} axis in the PS+PIB+benzene system. The inclination of the tie lines becomes more pronounced with decreasing temperature. This result reflects the fact that phase separation occurs at lower temperature even in the PS+CH binary sub-system in the former and in the PIB+benzene sub-system in the latter. It can be said that the solvent quality governs the compositions of the two conjugate phases in equilibrium.

For both systems, the predicted binodal curves are in almost quantitative agreement with the observed ones and the calculated tie lines change their direction with temperature in the same way as do the experimental ones. The calculations also correctly describe the variation of the shape of the binodal curves and the direction of the tie lines with the solvent used. This implies that the χ expressions for these ternary systems correctly account for the solvent affinity to the two polymer components. Our χ_{12} implicitly include the solvent property, since it represents the polymer-polymer interaction in a given solvent as can be understood from eqs 14 and 17. Equation 39 combined with relations 40 and 41 shows that χ_{12} at finite ϕ increases in CH but decreases in benzene with increasing ξ_1 ($=\xi_{PS}$) in the ternary systems containing the same PS+PIB mixture. It may be concluded that χ_{12} at a finite concentration increases with increasing composition of the polymer component for which the solvent used is poor.

II. Polystyrene+Cyclohexane+*N, N* Dimethylformamide

a. Interaction Functions

For this ternary system, the intraction function $\chi_{11}(\phi_1)$ for the PS+CH binary

sub-system is already given by eqs 30 through 35. The light scattering method cannot be applied to the sub-system CH+DMF to evaluate χ_{22} , since refractive index increment is negligibly small in this system. The required interaction function $\chi_{22}(\phi_2)$ was therefore inferred from the binodal data obtained experimentally: The binary solution consisting of CH and DMF phase-separates below about 46°C.^{24,25)} In so doing, we resorted to the nonrandom two-liquid (NRTL) equation by Renon and Prausnitz²⁶⁾

$$(\mu_0 - \mu_0^0)/RT = \ln(1 - x_2) + x_2^2 \left\{ \frac{\tau_{10} U_1^2}{[(1 - x_2) + x_2 U_1]^2} + \frac{\tau_{01} U_0}{[x_2 + (1 - x_2) U_0]^2} \right\} \quad (42)$$

$$(\mu_2 - \mu_2^0)/RT = \ln x_2 + (1 - x_2)^2 \left\{ \frac{\tau_{01} U_0^2}{[x_2 + (1 - x_2) U_1]^2} + \frac{\tau_{10} U_0}{[(1 - x_2) + x_2 U_1]^2} \right\} \quad (43)$$

$$U_0 = \exp(-\alpha \tau_{01}), \quad U_1 = \exp(-\alpha \tau_{10}), \quad \alpha = -1 \quad (44)$$

where x_2 is the mole fraction of component 2 (DMF) in the binary system. Substitution of eq 42 into eq 4 gives $\chi_{22}(\phi_2)$ as

$$\begin{aligned} \chi_{22}(\phi_2) = & \frac{1}{\phi_2^2} \ln \frac{P_2}{(1 - \phi_2)P_2 + \phi_2} - \left(1 - \frac{1}{P_2}\right) \frac{1}{\phi_2} \\ & + \frac{\tau_{01} U_0^2}{[P_2(1 - \phi_2) + U_0 \phi_2]^2} + \frac{\tau_{10} U_1}{[P_2 U_1(1 - \phi_2) + \phi_2]^2} \end{aligned} \quad (45)$$

This equation includes two parameters τ_{10} and τ_{01} which are independent of composition of the solution. They were evaluated by the analysis of the observed phase separation data²⁵⁾ with eqs 42 and 43. The results are expressed by

$$\tau_{10} = 1.417 - 187/T, \quad \tau_{01} = -1.020 + 601/T \quad (46)$$

We note that the NRTL equation with eq 46 reasonably well explained the vapor pressure data by Geier et al.²⁷⁾ for the CH+DMF solution below 50°C.

The χ_{12} function was obtained from the light scattering data for the ternary system PS+CH+DMF compared with the values calculated by eq 18. Here a working equation for χ_{12} was assumed as

$$\chi_{12} = k_0 + (k_1 \xi_1 + k_2 \xi_2) \phi + (k_3 \xi_1^2 + k_4 \xi_1 \xi_2 + k_5 \xi_2^2) \phi^2 \quad (47)$$

to meet the experimental finding that the L function for the binary sub-system PS+DMF was at least a quadratic function of ξ_1 . The coefficients k_i determined therefrom are summarized as follows.²⁸⁾

$$\begin{aligned} k_0 &= 0.020 T - 5.25, & k_1 &= -0.068 T + 21.67, & k_2 &= -0.091 T + 27.10, \\ k_3 &= 0.026 T - 7.55, & k_4 &= 0.104 T - 30.85, & k_5 &= 0.080 T - 22.39 \end{aligned} \quad (48)$$

Figures 4 and 5 compare the calculated and measured values of $KV_0 \phi / \Delta R_0$ or $KV_0 \phi_1 / \Delta R_0$ for the two series of the ternary solutions; one is located near the CH apex and the other near the DMF apex when their compositions are plotted on the composition triangle. In Figure 4, the data set at 35 and 25°C gives a curve bending downwards and approaches zero at high concentration, suggesting that the solution approaches the biphasic region. The calculations almost quantitatively reproduce the

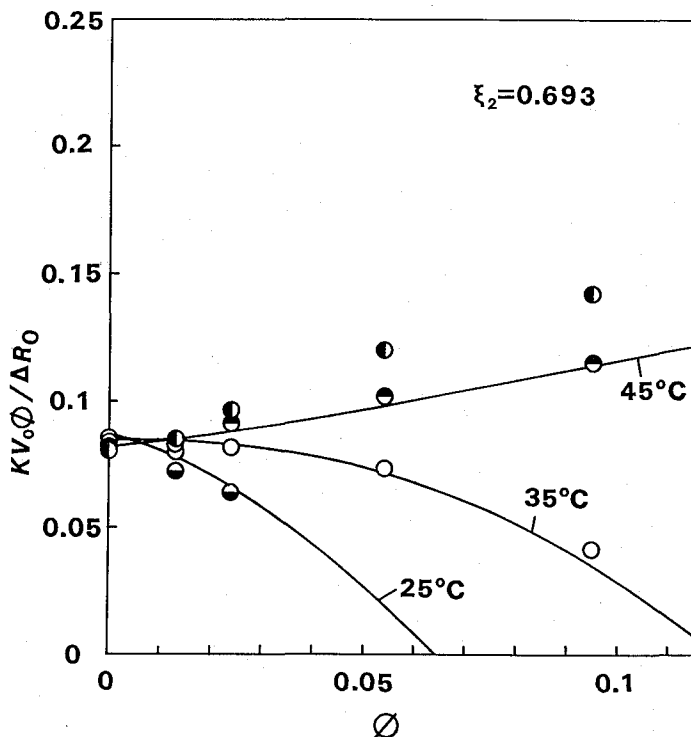


Figure 4. Plots of $KV_0\phi/\Delta R_0$ vs ϕ at $\xi_1=0.693$ for the PS (F4b)+CH+DMF system. \bullet , 25; \bullet , 35; \bullet , 45; \circ , 55°C. Solid lines, calculated values.

light scattering data below 45°C.

The ternary solutions in Figure 5 have nothing to do with phase separation. Values of $KV_0\phi_1/\Delta R_0$, thus, increases monotonically with increasing ϕ_1 at any temperature examined and do not significantly depend on temperature. Here, ζ denotes the composition of the solvent mixture CH+DMF, $\zeta=\phi_2/(\phi_0+\phi_2)$. The calculated results reasonably explain the ϕ_1 dependence of $KV_0\phi_1/\Delta R_0$ and their agreement with the experimental values is satisfactory below 35°C. However, the calculations give the temperature dependence of $KV_0\phi_1/\Delta R_0$ in a different way from the observations. This result suggests that our working equation for χ_{12} , i.e., eq 47, is not completely adequate to represent χ_{12} of the actual system over such a wide range of concentration as treated here.

b. Phase Diagram

The predicted binodal curves and tie lines are compared with the experimental data at 35 and 45°C in Figures 6 and 7, respectively. Overall resemblance of the calculated and observed results is apparent at a glance at either temperature. The tie lines in both results coincide with each other. They change their direction from the ϕ_1 ($=\phi_{PS}$) axis to the ϕ_2 ($=\phi_{DMF}$) axis with increasing ϕ_{PS} in the solution before phase separation, reflecting phase separation of the binary sub-system CH+DMF at these temperatures

Phase Equilibrium in Ternary Polymer Solution

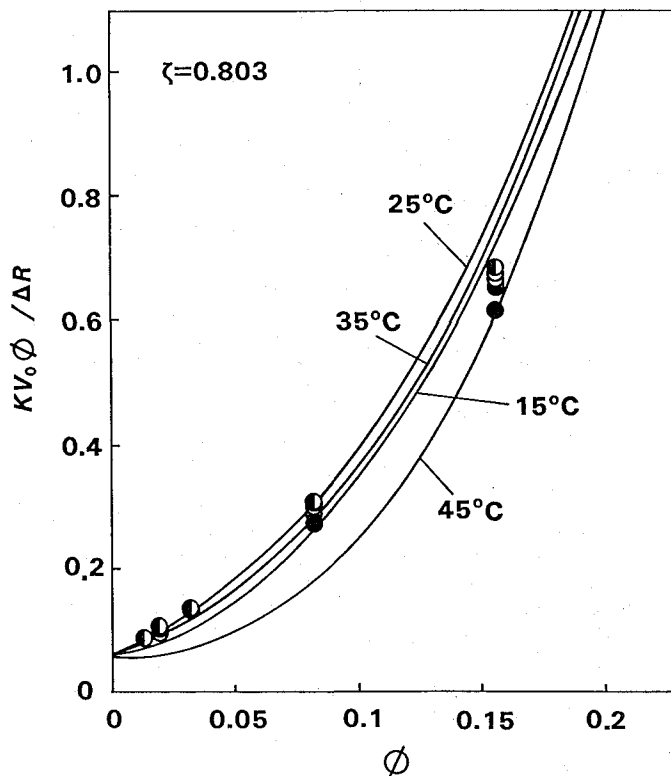


Figure 5. Plots of $KV_0\phi_1/\Delta R_0$ vs ϕ_1 at $\zeta=0.803$ for the PS (F4b)+CH+DMF system. ●, 15; ○, 25; ●, 35; ○, 45; ○, 55°C. Solid lines, calculated values.

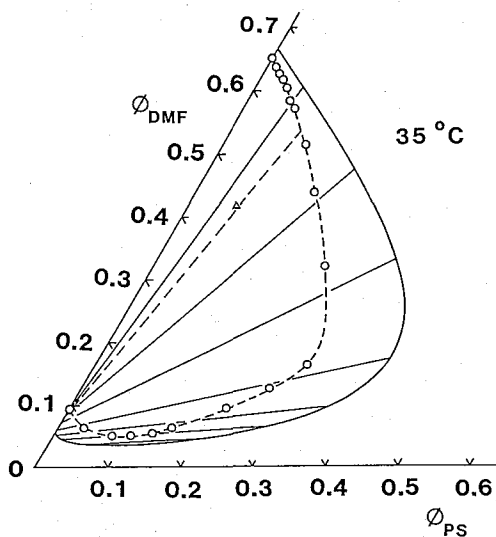


Figure 6. Comparison of the calculated and observed binodals and tie lines for the PS (F4b)+CH+DMF system at 35°C. Circles, observed binodals; dashed straight line, observed tie line; triangle, solution before phase separation; solid curve, calculated binodals; solid straight lines, calculated tie lines.

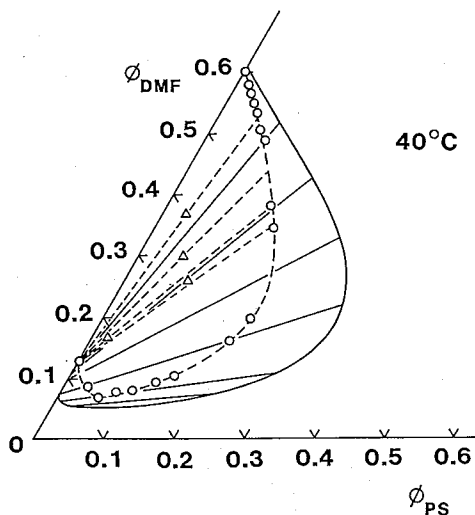


Figure 7. Comparison of the calculated and observed binodals and tie lines for the PS (F4b)+CH+DMF system at 40°C. Circles, observed binodals; dashed straight lines, observed tie lines; triangles, solution before phase separation; solid curve, calculated binodals; solid straight lines, calculated tie lines.

and of the binary sub-system PS+CH at lower temperatures. The calculated demixing region is correctly located in the composition triangle, extending from the ϕ_{DMF} axis to the direction of the ϕ_{PS} axis. Its agreement with the experimental results is, however, only moderate. This again indicates that the present expression of χ_{12} is too simpler than required.

CONCLUSION

In this work, our new approach to the phase problem in ternary polymer solutions was applied with reasonable success to the systems PS+PIB+CH, PS+PIB+benzene, and PS+CH+DMF. The results showed that the approach was useful in both the polymer+polymer+solvent and polymer+solvent+solvent ternary systems. It was, thus, proved that the present theoretical framework provides us with a powerful tool for establishing the dependence of the Gibbs free energy of mixing on all conceivable variables, thereby predicting the phase relationships of the relevant ternary system.

We also found that although the observed phase diagrams were correctly reproduced by the calculations, the agreement was not always precise enough in a quantitative sense. The agreement is improved if a more elaborated equation is employed for the χ_{12} function. It is, however, hesitant to proceed further at present when no information is available for the functional form of χ_{12} .

ACKNOWLEDGMENTS

This paper is based on the work performed at Osaka University Department of Macromolecular Science. The author is indebted to Dr. Z. Tong, Messrs. Y. Nakamura, T. Kitagawa, and T. Hirao for their assistance in the experimental work and numerical calculations. He wishes to express his sincere thanks to Professor Emeritus H. Fujita for his advice and helpful discussion.

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